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Applicability of Passive Monitoring Devices to Measurement of Volatile Organic Chemicals in Ambient Air

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Applicability of Passive Monitoring Devices to Measurement of Volatile Organic Chemicals in Ambient Air

by

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A high-performance passive device was developed for short-term, low-level monitoring applications. The stainless steel monitor is small, simply designed, and inexpensive. It has a high equivalent sampling rate, is reusable and rechargeable, and is amenable to thermal desorption. Laboratory and field tests with Tenax GC as the sorbent have shown that the monitor compares very favorably with active (pump-based) samplers.

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ABSTRACT

Commercial passive monitoring devices for volatile organic chemicals were evaluated to determine their potential application to ambient air concentrations (0.1 to 50 ppbv). Background interference, humidity and air velocity effects on sampling efficiency were examined. For one commercial device, it was demonstrated that blank levels can be limited to near or below analytical detection limits if extreme precautions are exercised. Chamber tests demonstrated that performance was independent of normal ambient air concentrations. High relative humidities (above 80%) and insufficient ventilation greatly impaired performance.

A high-performance passive device was developed for short-term, low-level monitoring applications. The stainless steel monitor is small, simply designed, and inexpensive. It has a high equivalent sampling rate, is reusable and rechargeable, and is amenable to thermal desorption. Laboratory and field tests with Tenax GC as the sorbent have shown that the monitor compares very favorably with active (pump-based) samplers.

INTRODUCTION

Personal monitoring devices have been used by industrial hygienists for many years to assess the effects of respiratory exposures to hazardous pollutants on workers. With the passage of the Clean Air Act in 1963, it became necessary to develop monitoring systems for ambient air to comply with air quality standards set to safeguard public health. Since ambient air levels of most pollutants are several orders of magnitude lower than those normally found in the workplace, more sensitive monitoring systems are required. These systems are generally not portable and are usually located at fixed, outdoor sites. Such fixed-site monitoring may not accurately reflect the average daily exposure of the general populace to air pollutants. This is particularly true in the United States, where the average person spends an estimated 90% of the time indoors[1].

To obtain an accurate estimate of individual exposure to air pollution, the person must carry or wear the monitor. Therefore, the device must be unobtrusive, lightweight, operate quietly, and place little or no burden on the individual. It must also be inexpensive, since much more equipment may be required for

personal monitoring than for fixed-station monitoring. Active (pump-based) sampling systems used for occupational exposure assessment can and have been used successfully outside of the workplace[2]. However, the pumps required weigh from 0.5 to 1.5 kg and may not be comfortable to wear, especially for small persons. In addition, they must be battery-powered and most cannot be continuously operated for more than 6 to 12 hr. Passive devices, which require no pump, are much lighter in weight and are not power-limited. They have the additional advantages of small size and relatively low cost, which make them ideally suited as personal-exposure monitors for toxic chemicals in air.

Passive air monitors may be either permeation- or diffusion-controlled. In each case, a collector or sorbent material is separated from the external environment by a physical barrier that determines the sampling characteristics of the device. Permeation-limited devices employ a membrane in which the test compounds are soluble. Because of this solubility requirement, it is possible to achieve some selectivity with permeation devices by choice of the membrane material. However, because of solubility variation even within a congeneric series of compounds, permeation devices must be calibrated for each individual chemical that is sampled.

With diffusion-limited devices, the collector is isolated from the environment by a porous barrier containing a well-defined series of channels or pores. The purpose of these channels is to provide a geometrically well-defined zone of essentially quiescent space through which mass transport is achieved solely by diffusion. As a general criterion for this condition, the length/diameter ratio (L/d) of the pores should be at least three. However, some investigators feel that the ratio should be at least eight[3]. Under such conditions, the mass flow rate to the collector is given by Fick's first law,

$$\dot{m} = (DA/L)(C_\infty - C_o),$$

where D is the diffusion coefficient for the compound of interest, A is the total channel area of the device, L is the channel length, C_∞ is the external concentration of the species, and C_o is the concentration at the surface of the collector. If the collector has any appreciable efficiency for sorption of the compound of interest, C_o is generally taken to be zero.

The quantity DA/L has units of volume/time. This quantity is often referred to as the sampling rate, analogous to that of active samplers. Preferably, the sampling rate of a given device should be determined independently before it is used for monitoring purposes. This is not usually practical, however, and one must rely on the manufacturer's specifications of A/L and/or DA/L. For most commercial diffusion-controlled devices,

the effective sampling rate is about 30 to 100 cm^3/min. Pump-based personal monitors may sample at rates up to 8,000 cm^3/min. Consequently, longer exposure times are often required for passive monitors in order to achieve equivalent sensitivities.

The effects of ambient temperature and pressure fluctuations on the sampling rates of passive devices may be estimated from the equation

$$D \propto \frac{T^{3/2}}{P} \quad ,$$

where T is absolute temperature and P is atmospheric pressure. Therefore, the theoretical temperature coefficient would be ~ 0.6% per °C and the pressure coefficient ~ 0.1% per mm Hg[4]. Humidity effects are less predictable, but may be pronounced for hydrophilic collectors or sorbents. Sampling rates are also dependent on the velocity of air movement over the face of the device, particularly if there are protrusions around the channel openings. The protrusions can contribute to the formation of boundary layers of stagnant air, which reduce uptake rates[4]. For chemicals that are weakly sorbed, significant equilibrium vapor pressures may exist at the face of the sorbent, which effectively reduce sampling rates according to Fick's law (i.e. $C_o > 0$).

Theoretical predictions suggest that the magnitude of this decrease will depend on ambient air concentrations[4]. Since most passive samplers have relatively large time constants (e.g., 11 s for benzene where L = 1 cm), and since the rates of migration into the sorbent bed are slow compared to the time constant, diffusional samplers may not respond accurately to rapidly fluctuating air concentrations. However, such fluctuations are not characteristic of pollutant levels in ambient air.

Despite the potential limitations of applying passive monitors to quantitatively measure air pollutants, these devices have in recent years been used quite successfully in occupational environments[5]. Their application to ambient atmospheres, which requires detection limits from 0.1 to 50 ppb, presents a greater challenge. The purpose of our investigations was to (a) determine whether commercially available passive monitors can be used to detect trace quantities of toxic organic chemicals in ambient air, and (b) to develop a thermally desorbable device with improved sensitivity for this task. These studies were conducted independently at Battelle Columbus Laboratories and Monsanto Research Corporation under the direction of the U.S. Environmental Protection Agency.

EXPERIMENTAL

Evaluation of Commercial Devices

The chamber used for commercial device exposure studies was a 200 L glass chamber constructed by joining two opposing bell jars to a central anodized aluminum ring. This ring was provided with numerous ports for loading, sampling, monitoring devices, etc. Stirring within the chamber was achieved by using a completely sealed internal fan that was magnetically coupled to an external variable speed drive unit. For these investigations, a stainless steel shroud and swirl dampener was placed over the fan to achieve well-directed flow within the chamber and a uniform laminar flow pattern near the devices.

The devices were loaded into the chamber using the sample holder shown in Figure 1. This holder was a stainless steel cylinder with a central rod for attachment of the devices. For a given experiment, the devices were attached to the holder under a protective clean atmosphere (glove box) and the cylinder was closed, flushed with zero-grade nitrogen, and inserted into the chamber. One end of the cylinder was locked in place while the other end protruded through a seal in the aluminum ring. The concentrations of test chemicals could then be adjusted in the chamber without exposure of the badges. At the start of a chamber exposure, the outer shell of the cylinder was partially withdrawn through the seal, leaving the devices suspended from the central

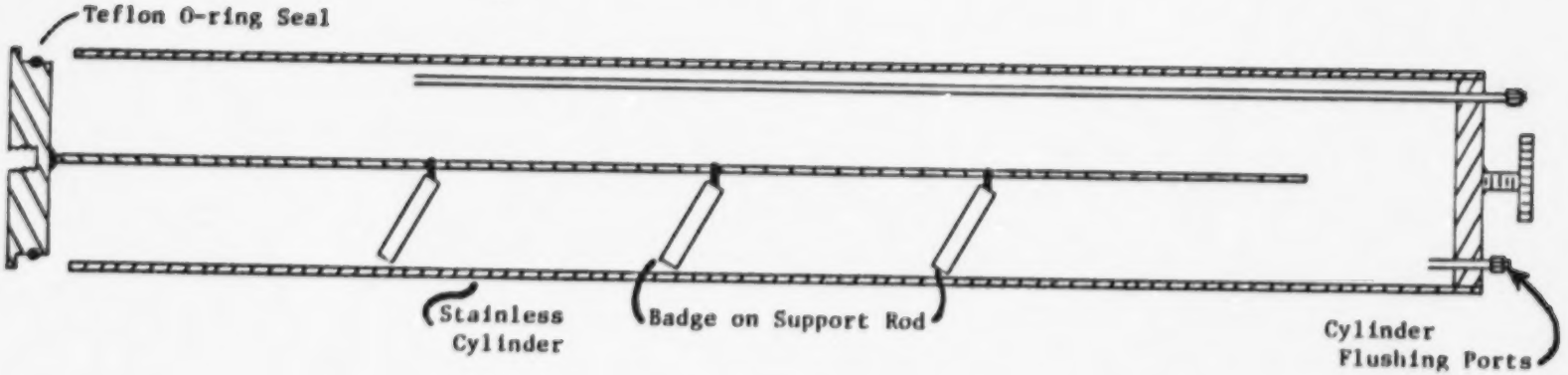


Figure 1. Loading and support device for exposure chamber testing of commercial passive monitors (Battelle Columbus Laboratories).

rod. At the completion of the trial, this procedure was reversed, and the entire assembly was removed to a glove box for disassembly and preparation of the collector for analysis.

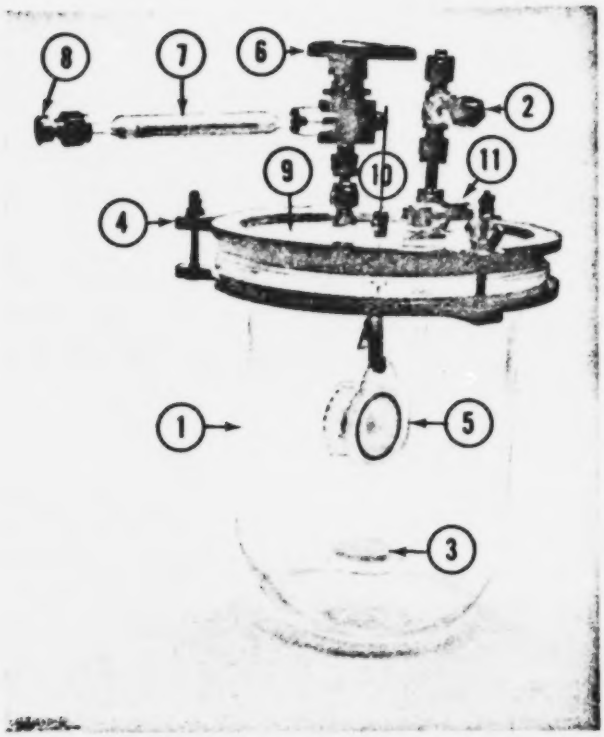
Prior to each chamber trial, the chamber was throughly flushed with zero-grade nitrogen, and direct gas analyses were made by gas chromatography (GC) to confirm the initial condition of the chamber. The test chemicals were added by directly injecting an appropriate liquid or gas mixture of the pure chemicals. Dilution then was carried out in the chamber as needed to obtain the desired concentrations. Once loaded, the chamber was operated in a dynamic mode and about 50 cm^3/min was removed for GC analysis. Appropriate makeup gas was added to maintain the chamber at about 25 mm H_2O above ambient pressure. Velocity measurements were made using an Alnor anemometer.

Exposed devices were extracted with 1 mL of 5% carbon disulfide in methanol as described previously[6]. All analyses were performed on a Varian 3700 gas chromatograph equipped with tandem electron capture and photoionization detectors, coupled with Hewlett-Packard 3390 integrators. Hewlett-Packard SE-30 coated fused-silica columns, 25 m and 50 m, were employed.

Development of New Devices

A laboratory test exposure chamber, shown in Figure 2, was designed and assembled to provide the required test conditions for testing and evaluating the thermally desorbable devices. Basically, the exposure chamber was a 2-L borosilicate glass reaction kettle fitted with an "O"-ring-sealed Teflon lid. A standard clamp ring sealed the lid to the vessel.

Three ports were provided through the chamber lid; one port was used to admit test gas mixtures into the chamber. Gas line connections were made through appropriate Swagelok® fittings. The gas inlet line terminated into a coarse glass frit which promoted a more even gas flow distribution within the chamber, thus minimizing channeling effects. A second port provided an access for inserting probes to monitor temperature and humidity within the chamber during test runs. Environmental conditions such as temperature and humidity could be selected and maintained over a broad range, thus providing means for evaluating passive monitor performance with respect to given environmental parameters. The third port of the system was fitted with a 3-way ball-valve to direct the gas effluent from the exposure chamber to either the vent or sample position. Sorbent tubes were used to collect known volumes of sample to validate gas constituent(s) concentrations within the chamber during trails. Test devices were suspended above the glass frit during the exposure period. The distance



1. Glass exposure chamber
2. Gas inlet fitting
3. Glass frit
4. Clamp ring
5. Monitor under test
6. Vent - sample selection valve
7. Sorbent sample tube
8. Probe inlet
9. Teflon lid
10. Device hanger
11. Connection to sample pump

Figure 2. Exposure chamber for testing and evaluation of thermally desorbable passive monitors (Monsanto Research Corporation).

between the device and gas entrance could be selected and maintained constant.

A three-stage, syringe-driven gas dilution system was used to provide test atmospheres of known concentrations into the exposure chamber. Nitrogen was used as the carrier gas, and flows were accurately measured by Brooks Model 5841 mass-flow sensor/controllers. Precision pressure gauges (Heise Model CM) were used to maintain a constant pressure differential between stages. A five-port manifold system was used to split out a portion of the flow for sampling.

After exposure, the passive monitors and active sampling tubes were thermally desorbed separately under helium purge into a cryogenic trap (77°K), which was in turn resistively heated to transfer the trapped material to the GC column. The assembly, shown in Figure 3, was designed to handle the desorption of sampling tubes (dynamic flow) as well as the passive devices. The unit was equipped with two manually operated 6-port, high temperature (300°C max.) Valco® valves. "Switching valve" #1 directed helium purge gas through either the sorbent tube or the passive monitor to a second valve used to select the "desorb/trap" or "analyze" mode of operation. The "desorb/trap" mode diverted the purge gas through a cryogenically cooled sample loop to provide off-line trapping, which in addition provided better carrier gas flow rate control. When valve #2 was switched to

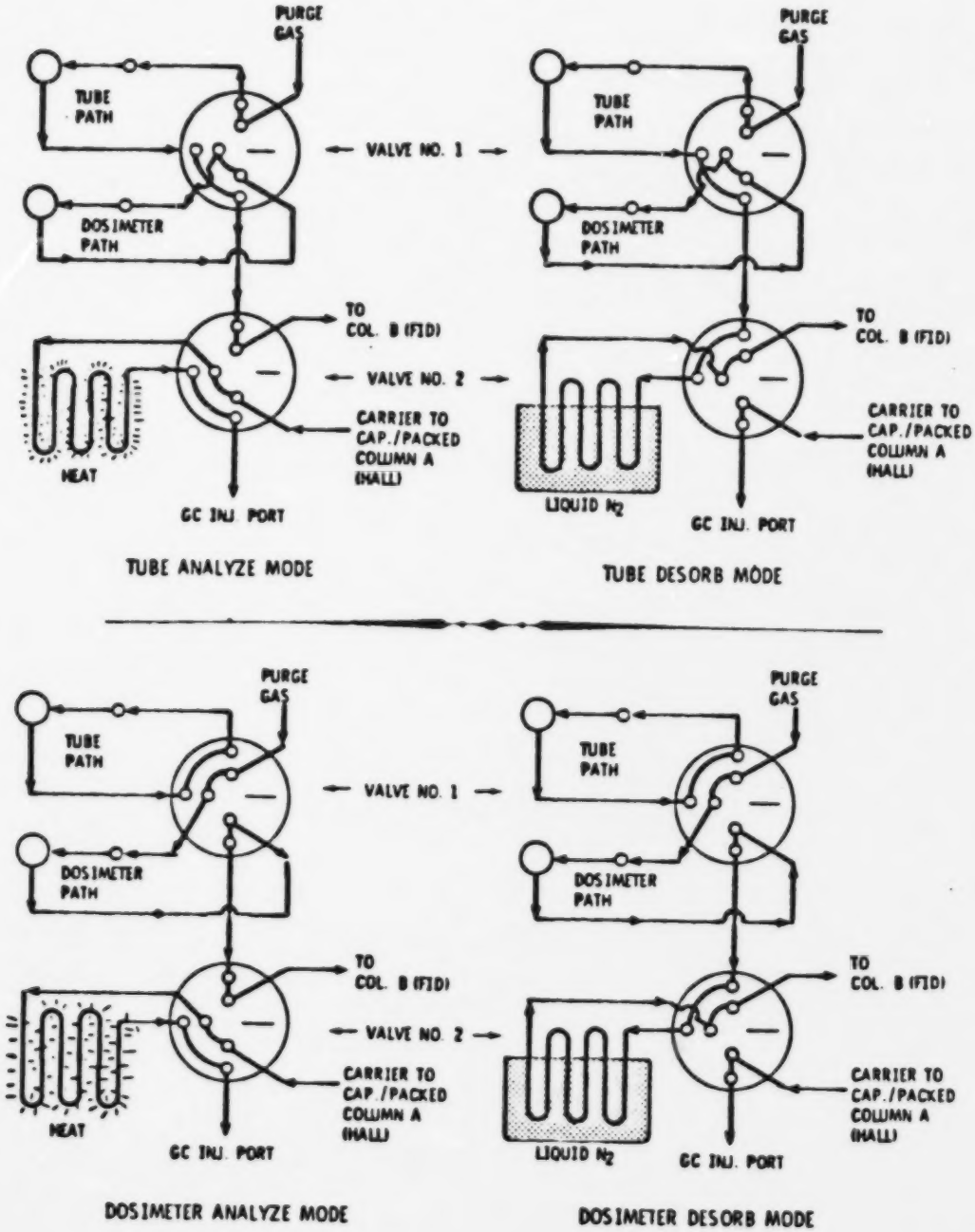


Figure 3. Thermal desorption/trap unit schematic.

the "analyze" mode, a second gas stream (helium carrier gas) was backflushed through the sample loop, which was then ballistically heated to rapidly deliver the trapped compounds to the analytical column for gas chromatographic analysis.

A Hewlett-Packard 5711 gas chromatograph equipped with a Hall microelectrolytic conductivity detector (Tracor 700) and an HNu photoionization detector was used. A 2 mm (i.d.) x 243 cm glass column packed with 1% SP 1000 on 60-80 mesh Carbopak B was heated from 60° to 210°C at 8°/min and held at the upper temperature for 15 min for most analyses.

RESULTS AND DISCUSSION

Evaluation of Commercial Devices

In a previous study conducted by Battelle Columbus Laboratories for the U.S. EPA, three commercially available passive organic vapor monitors were evaluated for their potential application to ambient air monitoring[6]. These were the Gasbadge® Organic Vapor Dosimeter (Abcor Development Corporation, Wilmington, MA), which was the first passive personal monitor marketed for organic chemicals; the 3M Brand Organic Vapor Monitor, Type 3500 (3M, St. Paul, MN) and the Pro-Tek® Air Monitoring Badge, Type G-AA (E.I. duPont de Nemours and Co., Inc., Wilmington, DE). All three are diffusion controlled, with the first two depending on gaseous diffusion through porous filters or membranes, while the last employs an array of open channels 1 mm in diameter and 3 mm in length. Activated charcoal is used as the sorbent in each of the devices. The objective of the study was to determine the applicability of these passive monitors to 24-hr monitoring of multiple volatile organic compounds at typical ambient atmospheric levels. Seven representative volatile toxic chemicals relevant to the U.S. EPA monitoring requirements were chosen as test chemicals. These were chloroform, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, tetrachloroethylene, benzene, and chlorobenzene.

The technical problem faced was the achievement of quantitative detection limits of 0.1 ppbv or less (~0.4 $\mu g/m^3$) for devices designed to monitor air pollutants in the parts-per-million range. At a typical sampling rate of 50 cm^3/min and a 24-hr exposure, these devices would accumulate only 30 ng of material. Analytical requirements for reliable detection at this level would then permit blank levels of ~ 3 ng. Blank levels of the test compound, as supplied by each of the manufacturers, were considerably in excess of this value[6]. However, through a cooperative arrangement, duPont was able to furnish thermally cleaned Pro-Tek G-AA badges with blank values of < 0.1 to < 18 ng/badge for the seven test compounds. These levels were equal to or less than the extraction solvent blanks for the compounds. Extensive laboratory testing was then conducted to refine analytical techniques, identify potential interferences and determine the effects of concentration, relative humidity, and air velocity on the performance of the duPont badge.

Most of these studies were carried out in the 200-L glass chamber described in the Experimental Section. A limited amount of performance evaluation was conducted in real atmospheres (in the laboratory). Chamber tests were conducted at nominal time-weighted average (TWA) concentrations (0.03 to 50 ppbv), exposure times of 4 to 21 hr, and relative humidities of 7 to 92%. Air flow velocities were 40 to 60 cm/s (80-120 ft/min) in all

experiments. Temperature and air velocity effects were not directly measured in the chamber studies, but were estimated theoretically.

In addition, tests were conducted in the laboratory to verify the calculated velocity effects. The Pro-Tek G-AA badges were exposed (both faces) in triplicate under each set of chamber conditions. The mean responses relative to the directly measured chamber gas concentrations (R = device measured conc./TWA chamber conc.) are given in Table I. While the mean relative response $\bar{R}$ is good for all chemicals except carbon tetrachloride, the badge-to-badge variation was found to be undesirably high. Close examination of individual badge data revealed that when a high response was observed for one chemical, the responses for the other chemicals were also high. Individual responses correlated well with mean responses for each badge, suggesting that the observed variations were largely due to variations in the sampling rates of the devices. The apparent contribution of the sampling rate variations to overall data variance was much larger than that suggested by Lautenberger et al.[7] Therefore, 30 of the diffuser plates taken from badges used in this study were examined closely for structural differences. The thickness of the plates and the volumes of the channels were determined, and the ratio of channel area to channel length was then calculated for each plate. The relative standard deviation for these measurements was 0.055,

Table I. Mean relative responses of duPont Pro-Tek® G-AA Badges

Chemical	Number of Trials[a]	Chamber TWA Conc. Range (ppbv)	Mean Relative Response[b] Uncorrected $\bar{R}$	Uncorrected σ	Corrected[c] $\bar{R}$	Corrected σ
Chloroform	8	1.7 - 4.6	0.83	0.33	0.76	0.21
1,1,1-Trichloroethane	7	2.2 - 10.4	1.11	0.36	1.02	0.24
Carbon tetrachloride	8	0.037- 13.8	0.65	0.29	0.57	0.23
Trichloroethylene	8	0.32- 21.2	0.97	0.36	0.90	0.29
Tetrachloroethylene	8	0.34- 35.0	0.86	0.39	0.77	0.28
Benzene	3	2.4 - 5.8	0.81	0.48	0.66	0.25
Chlorobenzene	4	1.1 - 48.7	0.83	0.76	0.76	0.19

[a]Three badges were exposed during each trial. Tests were conducted at 7, 11, 72, 80 and 92% relative humidities.
[b]Ratio of apparent concentration measured by badge to directly measured gas phase TWA concentration.
[c]Corrected by exclusion of two badges which gave abnormally high responses (> 1.5).

which agrees with Lautenberger's estimate of 0.05. Thus the observed variations in apparent sampling rate must be due to some factor other than A/L, and may indicate poor seals between the plates for those badges showing very high responses. When the two badges which exhibited responses 1.5 to 3 times greater than the other badges for all chemicals are deleted, the corrected average response data (Table I, column 5) show somewhat better precision.

Very low responses were obtained in two trials conducted at 80 and 92% relative humidity. As can be seen in Table II, average responses decreased 30 to 60% under conditions of high humidity. The isotherms for sorption and desorption of water by the duPont badge are shown in Figure 4. The observed isotherm is a type V isotherm that is fairly typical of water absorption by charcoals. This type of isotherm generally indicates little adsorption, but extensive capillary condensation of the sorbate. Hysteresis, as shown in Figure 4, also is expected. At about 80% relative humidity, the pore space of the duPont badge is 90 to 95% filled with water (depending on the direction of approach), and it is therefore not surprising that apparent sampling rates are diminished at this point.

The remaining variations in the data can be attributed largely to analytical error. Each response ratio was derived from

Table II. Effect of high humidity on response of duPont badges

Chemical	Mean Relative Response (corrected)[a] At 7-72% RH[b] $\bar{R}$	σ	At 80-92% RH $\bar{R}$	σ
Chloroform	0.85	0.11	0.44	0.02
1,1,1-Trichloroethane	1.09	0.18	0.69[c]	0.28
Carbon tetrachloride	0.67	0.17	0.27	0.03
Trichloroethylene	1.00	0.26	0.58	0.14
Tetrachloroethylene	0.89	0.20	0.39	0.04
Benzene	0.79	0.15	0.35[c]	0.01
Chlorobenzene	0.84	0.20	0.69[d]	0.17

[a]Corrected by exclusion of two badges which gave abnormally high responses.
[b]Average of 16 badges, except 5 badges each for benzene and chlorobenzene.
[c]Average of 2 badges at 92% RH only.
[d]Average of 3 badges at 80% RH and 2 badges at 92% RH.

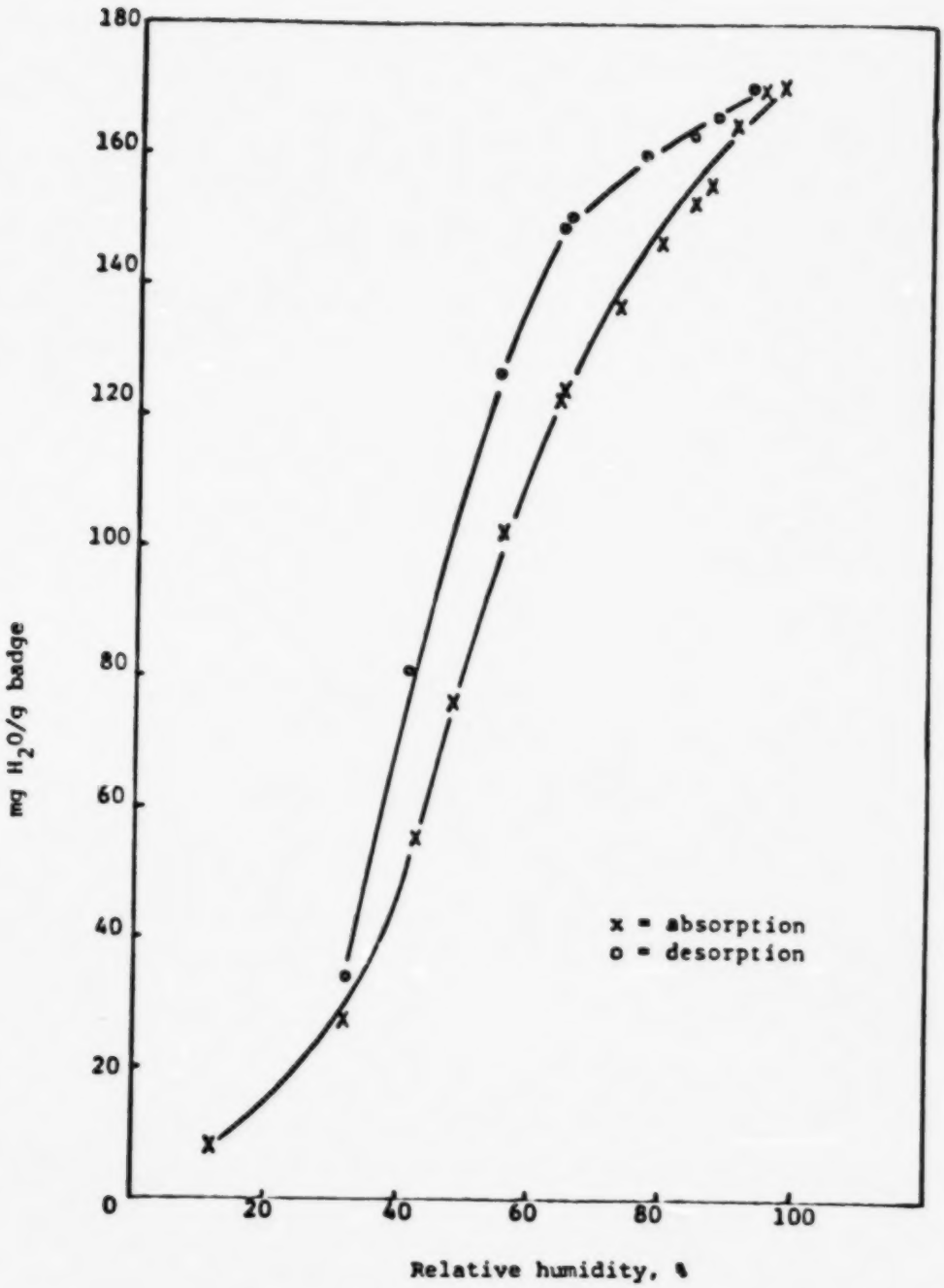


Figure 4. Sorption of water by duPont badge at 25°C.

analysis of two different samples, badge and gas, and the precision associated with each was found to be approximately ±5%. Exceptions appear in the cases of 1,1,1-trichloroethane, benzene and chlorobenzene. For the latter two chemicals, only limited data were obtained, however, because of analytical problems encountered. With 1,1,1-trichloroethane, and with benzene to a lesser extent, spurious contamination of laboratory air, standards, and solvents was a frequent problem and may have caused the observed variation. Although high humidity adversely affected the performance of the duPont badge, badge response was acceptably accurate at humidities < 80% for all of the test chemicals.

Air velocity effects were first considered on a theoretical basis. The physical mechanism whereby passive monitors achieve effectively constant volumetric sampling rates is determined by the use of a well-defined diffusion path between the collection medium and the external environment. The relationships generally cited for calculation of badge sampling rates assume that the gas-phase concentration of a given species is at the environmental level (C_∞) at the outer surface of the monitoring device. This assumption is never exactly correct but is compensated for by experimental determinations of sampling rates by the manufacturers. Such rates, however, are useful only when the external gas velocity is sufficient to bring the gas species to

the outer surface of the badge at least as fast as they are depleted by diffusion to the collection medium. The importance of the gas velocity has been demonstrated experimentally by Lautenberger et al.[7], at duPont and, as is shown below, their results are consistent with a simple aerodynamic model of mass transfer to the badge.

Consider the system indicated by Figure 5 where a collector is separated from the external air by a series of channels having length x and a total open area of A_o. The flow of air over the surface of the channels (sampling surface) will tend to result in the formation of a relatively stagnant boundary layer between the monitoring and the bulk air. Mass fluxes from the bulk air to the surface of the device (J_2) and from the surface to the collector (J_1) are given by Fick's first law,

$$J_1 = D\left(\frac{dC}{dx}\right)_{o\to x} = D\left(\frac{C_x - C_o}{x}\right)$$

and

$$J_2 = D\left(\frac{dC}{dx}\right)_{x\to\delta} = D\left(\frac{C_\infty - C_x}{\delta}\right),$$

where D is the diffusion coefficient for a given species. If the total face area of the device is A_b and C_o is taken to be zero, the mass transfer rates can be written as

$$\dot{m}_1 = \left(\frac{A_o}{x}\right) D \cdot C_x$$

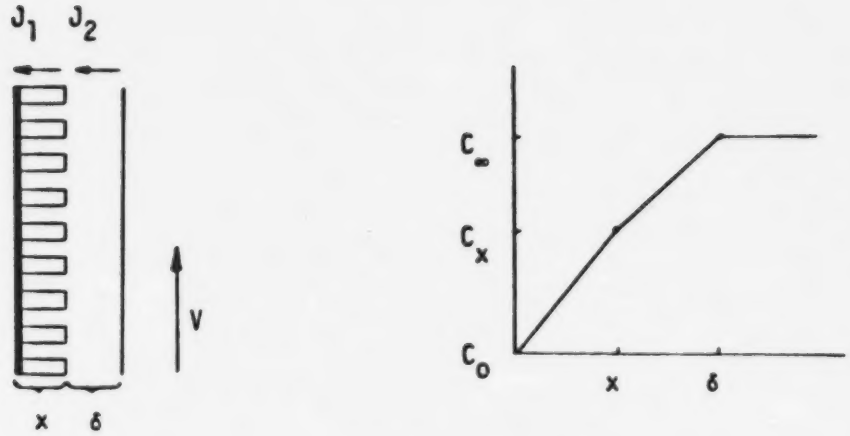


Figure 5. Effects of boundary layer over badge surface.

and

$$\dot{m}_2 = \frac{A_b}{\delta} D (C_\infty - C_x).$$

Because $A_o/A_b = \varepsilon$, the effective porosity of the sampling surface, and because in a steady-state sampling condition $\dot{m}_1 = \dot{m}_2$, then

$$\frac{C_x}{C_\infty - C_x} = \frac{x}{\varepsilon\delta}$$

or

$$\frac{C_x}{C_\infty} = \frac{x/\varepsilon\delta}{1 + x/\varepsilon\delta} .$$

Now δ is a function of the air velocity and the badge dimensions, and is defined[8] as:

$$\delta = 3.46\sqrt{\frac{\mu\ell}{V\rho}} ,$$

where μ is the viscosity, ℓ is the distance from the leading edge of the surface, and ρ is the density of the air. Using the dimensions of the duPont badge,

$$x = 0.35 \text{ cm}, \ \varepsilon = 0.3, \ \ell = 0.5 \text{ cm},$$

$$\rho = 1.2 \times 10^{-3} \text{ g/cm}^3, \ \mu = 1.85 \times 10^{-4} \text{ poise}$$

$$(V = \text{cm/s}),$$

then

$$\frac{C_x}{C_\infty} = \frac{0.36 \ V^{1/2}}{\varepsilon + 0.36 \ V^{1/2}}$$

Because it is normally assumed that $C_x \sim C_\infty$, this equation indicates that absolute accuracy of the sampling rate is a function of velocity. A plot of this function is shown in Figure 6.

The need for calibration of effective sampling rates by the manufacturer is made obvious by Figure 6. C_x approaches C_∞ only at very high velocities. However, C_x is relatively independent of velocity above some arbitrary minimum, for example, 25 cm/s. Below about 25 cm/s, and certainly below 15 cm/s, the steady-state sampling rate is a function of velocity. This behavior is essentially the same as noted by Lautenberger et al.[7], except they assumed a constant rate at high velocities.

From a practical viewpoint, Figure 6 illustrates a potentially serious fault of the duPont passive monitor. Although velocities of 25 to 50 cm/s are routinely generated by movement of an active person, such velocities may not be attained by an office worker or a subject not engaged in vigorous activity. Velocity measurements conducted at a variety of sites in the investigators' laboratories generally were below 15 cm/s unless either direct exposure to ventilation or movement at walking speeds was involved. This problem may be further compounded by the shielding effect of the body and clothing when the badge is worn close to the body (as opposed to being attached to an extremity).

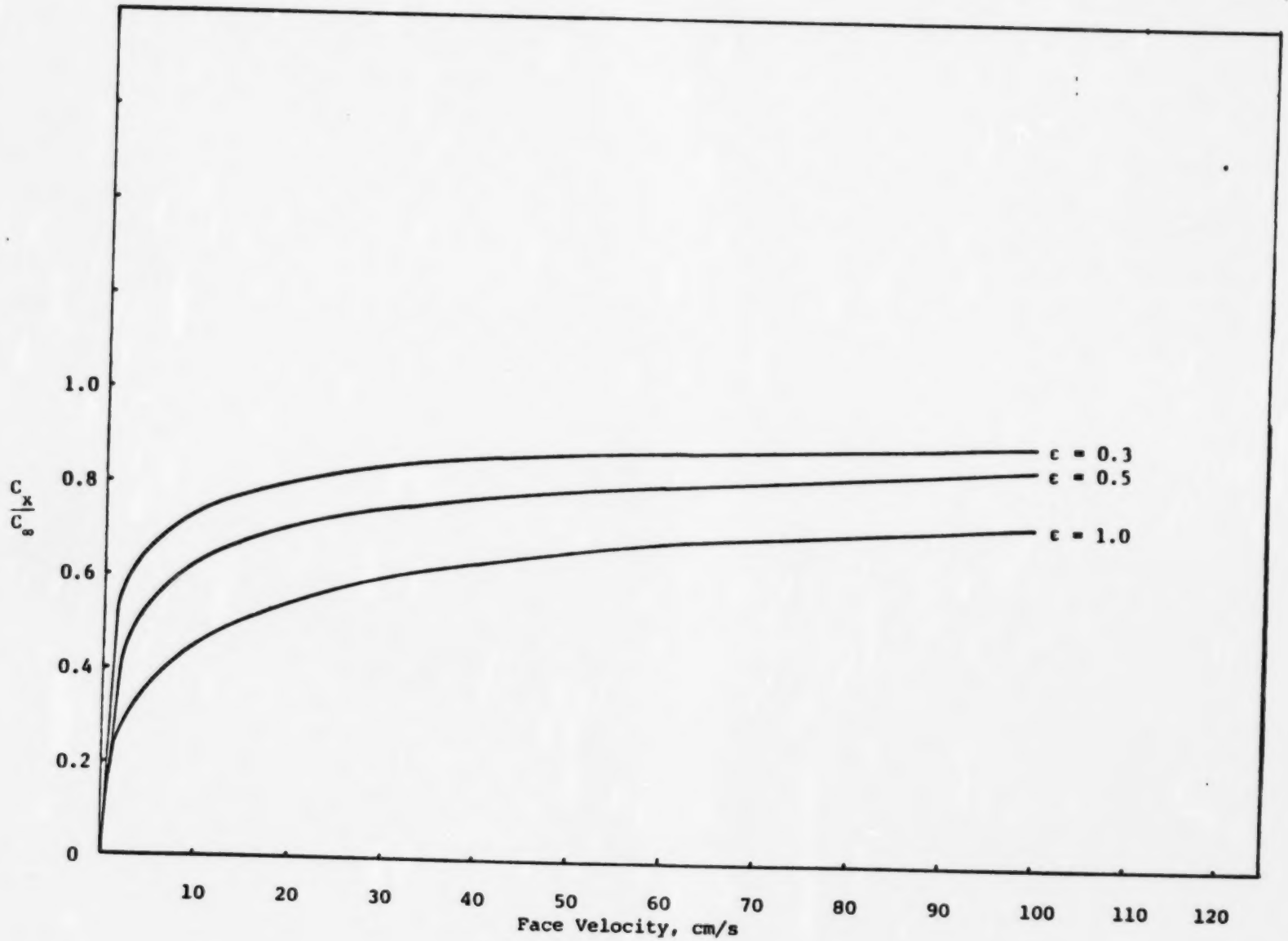


Figure 6. Theoretical effects of air velocity on sampling rates.

To test this premise, we exposed four duPont badges to laboratory air for 8 hr. Two were suspended in front of a small blower which forced air at about 60 cm/s over the faces of the devices. The other two badges were suspended within an open beaker to minimize convective air transport. Results of this experiment are shown in Table III. The suspension of the badges within beakers did not totally inhibit air transport to the badges, but instead limited transport by redefinition of the diffusion path. The overall sampling rate should have been decreased by about 50% because of the beaker size and geometry. Values reported in Table III are in reasonably good agreement with this anticipated reduction.

The effects of temperature on diffusion-limited devices were not measured explicitly. Although kinetic gas theory suggests that the diffusion coefficient is proportional to $T^{1.5}$ (see Introduction), empirical correlations, such as those described by Fuller et al.[9], usually show better results if $T^{1.75}$ is used.

Factors affecting the precision and accuracy of duPont badges are shown in Table IV. Estimated coefficients of variation given in this table are based on repeatability of analysis, estimated temperature and velocity effects, and apparent variations in sampling rates. Analysis of individual badge data using the definitions precision and accuracy given by Lautenberger et al.[7], yields similar values for the overall accuracy and slightly lower

Table III. Effect of air velocity on duPont badges

Compound	Apparent TWA Concentrations (ppbv)[a]	
	At 60 cm/s	At ≈ 0 cm/s
Chloroform	0.8	-
1,1,1-Trichloroethane	815	554
Carbon tetrachloride	0.9	0.5
Trichloroethylene	27	18
Tetrachloroethylene	8.6	4.5
Benzene	7.0	2.0
Chlorobenzene	< 0.3	< 0.3

[a]Exposure time = 8 hr; relative humidity = 21%; temperature = 22.5°C.

Table IV. Factors affecting precision and accuracy of duPont badges

Sources of Error	Estimated CV[a]	Affected Measure	
		Precision	Accuracy
1. Analysis Method			
a. Solvent blank	0.05	X[b]	X[b]
b. Desorption efficiency	0.10		X
c. Sample analysis	0.05	X	X
2. Sampling Conditions			
a. Velocity	0.04		X
b. Temperature	0.03		X
3. Device Characteristics			
a. Badge blank	0.05	X[b]	X[b]
b. Sampling rate	0.055	X	X
Total contribution, Σ(CV)		0.11 - 0.20	0.28 - 0.38

[a]Coefficient of variation = standard deviation/mean.
[b]Maximum contribution of blanks; if blank is much smaller than sample, contribution will be less.

values for the overall mean coefficients of variation. Results of this analysis are shown in Table V. These data again reflect the earlier observation that improved reference sampling rates, especially in the case of carbon tetrachloride, should improve the overall accuracy considerably. If the data are normalized, the overall accuracy is improved by an average of 0.25 ± 0.09 for the first five compounds, which stresses the contribution of variation to the badge sampling rate.

Because of the potential for improving detection limits by use of thermal desorption, this technique was applied to many of the samples generated in the chamber tests. Small portions (≈ 1/40) of the solvent strips were cut for thermal desorption, while the bulk of the strip was subjected to solvent desorption. Subsequent analytical results were corrected for the mass of the particular sorbent strip used. Segments that were analyzed by thermal desorption were inserted into a standard glass GC injection port liner that could then be placed in a spare injector. This injector was equipped with a rapid-rise heater and temperature readout system that was separate from the normal GC system. Samples were heated to 300°C for 10 min and the vapors were cryogenically trapped on-column. This temperature is that used by the manufacturer for thermal cleanup of the devices. The results of these studies, given in Table VI, show that none of the

Table V. Experimental precision and accuracy for duPont badges at 7 to 70% relative humidity

Chemical	Mean CV[a]	Mean Bias[b]	Overall Accuracy[c]
Chloroform	0.15	-0.11	0.41
1,1,1-Trichloroethane	0.15	0.14	0.45
Carbon tetrachloride	0.16	-0.30	0.63
Trichloroethylene	0.17	0.03	0.37
Tetrachloroethylene	0.22	-0.06	0.51
Benzene	0.10[d]	-0.21	0.42
Chlorobenzene	0.26	-0.09	0.61

[a]Based on all data except that generated at 80 and 92% RH.
[b]Group mean value of run mean deviation from response of unity.
[c]Overall accuracy = absolute mean bias + 2 (mean CV).
[d]Limited data.

Table VI. Solvent vs thermal desorption for duPont badges

Compound	Average Concentration (Range) in ppbv		
	Chamber	Solvent Desorption	Thermal Desorption
Chloroform	0.297	0.242(0.235-0.267)	0.014(0.011-0.018)
Carbon tetrachloride	0.037	0.030(0.029-0.031)	0.000
1,1,1-Trichloroethane	3.94	3.68 (3.47 -3.83)	0.26 (0.21 -0.31)
Trichloroethylene	0.226	0.327(0.312-0.341)	0.15 (0.09 -0.25)
Tetrachloroethylene	0.247	0.235(0.232-0.238)	0.14 (0.05 -0.25)
Benzene	0.264	1.96 (0.50 -4.4)[a]	0.15 (0.29 -0.65)
Chlorobenzene	0.132	ND	0.172(0.110-0.246)

[a]Solvent blank problems.

test chemicals could be efficiently thermally desorbed, with the possible exception of chlorobenzene.

Sampling rates published by duPont for the G-AA badge (dual face exposure) agreed well with those calculated using the diffusion coefficients estimated by the procedure of Reid et al.[10] and the empirical correlation of Fuller et al.[9] (see Table VII). Table VII also shows the estimated limits of detection for a 24-hr exposure. These detection limits are generally adequate to monitor ambient levels of the chemicals.

Development of a Thermally Desorbed Device

The high-performance passive exposure device shown in Figure 7 was developed by the Monsanto Research Corporation (MRC) under contract to the U.S. EPA. It was evaluated as a monitor for volatile organics in ambient air and for short-term, low-level measurement of toxic air pollutants near hazardous waste disposal sites. The device (and its parts) is constructed of stainless steel, measures 3.81 cm in diameter, 1.27 cm in depth, and weighs 36 g. In comparison, the duPont Pro-Tek G-AA badge weighs 12 g, and the Abcor-Gasbadge weighs over 40 g. Both are constructed of plastic. Like the G-AA badge, the MRC dosimeter can be used in either the single- or dual-face exposure modes. Polyethylene caps (Caplug EC-24, Protective Closure Co., Buffalo, NY)

Table VII. Sampling rates and lower useful detection limits for duPont badge[a]

Compound	Sampling Rate cm^3/min		C_{LL}[c] (ppbv)	Limiting Factor
	Published[b]	Calculated		
Chloroform	79	81	0.11	Detection
1,1,1-Trichloroethane	60	73	0.13	Blank/Detection
Carbon tetrachloride	74	73	0.01	Detection
Trichloroethylene	65	74	0.13	Blank/Detection
Tetrachloroethylene	51	68	0.02	Detection
Benzene	71	79	0.65	Detection
Chlorobenzene	66	71	2.5	Detection

[a]24-hr sampling period.
[b]As cited by duPont brochure, May 1981. Rate is with both covers removed.
[c]Lower limit of detection.

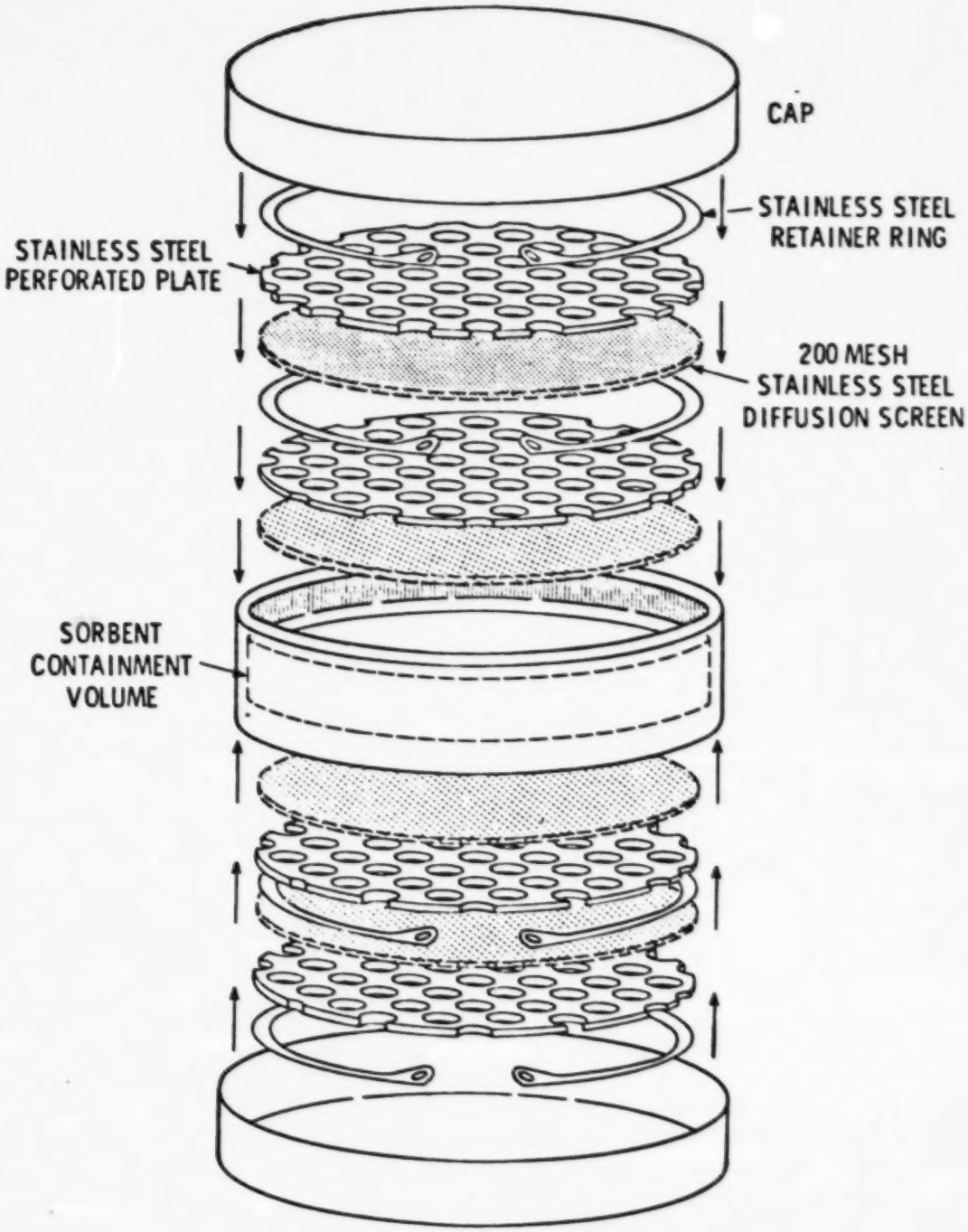


Figure 7. MRC thermally desorbable passive dosimeter.

are used to seal one face for single side exposure, or both faces to terminate sampling. The internal diameter of the body is 3.5 cm, except for the central portion, which is reduced to 3.0 cm to provide a precisely defined containment volume for the sorbent. Pairs of 200-mesh (33.6% open area) wire screens and perforated plates (1.0-mm diameter holes, 35 holes/cm^2, 28% open area), placed on each side of the sorbent bed, serve as diffusion barriers.

Any type of sorbent may be used in the device. However, the sorbent used in this study was Tenax GC (Enka NV, The Netherlands); about 0.4 g was required to fill the cavity. The device may be easily assembled and disassembled with snap ring pliers and reused with the same sorbent indefinitely. After use, the dosimeter is thermally desorbed in a specially contructed oven and the material is routed into a cryogenic trap for subsequent release into the gas chromatograph. Through an arrangement of switching valves, both the passive monitors and Tenax tubes from active sampling devices could be compared sequentially in this study (see Experimental Section).

A comprehensive laboratory study was conducted to establish the MRC dosimeter response to varying concentrations of test compounds. Initially, the devices were fortified by liquid injection of standard onto the sorbent, thermally desorbed, and analyzed. A linear response was obtained for each compound over a

range from 10 to 60 ng/device (corresponding to that expected at common ambient air concentrations). In addition to liquid fortification, the dosimeters were also fortified with gas standards from the MRC sample generation system (see Experimental Section). A series of test compounds were generated in gaseous phases at three dilution stages as given in Table VIII. One-hour dosimeter exposures to 1 ppb levels resulted in the collection of approximately 30 ng of each compound. Sample loadings considerably smaller than 30 ng could be detected with a high degree of confidence, thereby indicating a dosimeter sensitivity considerably below 1 ppb. The GC detection limit with the Hall® microelectrolytic conductivity detector was approximately 10 pg. The practical analytical detection limit was about 1 ng.

To evaluate the sampling performance of the MRC dosimeter, direct comparisons between the dosimeter and active sorbent sampling tubes were made. Comparisons were made by exposing dosimeters in the exposure chamber to various gas mixtures and sampling simultaneously with a sampling tube packed with Tenax GC. Tubes and dosimeters were then analyzed to determine the amount of material collected. The volume of gas passing through the sorbent sampling tube was measured during each trial. The equivalent sampling rate for the dosimeter was determined by dividing the mass of material collected by the mass-to-volume ratio determined

Table VIII. MRC sample generation system summary

Compound	Density g/cm^3	Molecular weight	Concentration g/mL	Concentration, ppm		
				Stage 1	Stage 2	Stage 3
Chloroform	1.492	119.39	0.1625	9.39	0.12	0.0012
1,2-Dichloroethane	1.256	98.97	0.1624	11.32	0.14	0.0014
Carbon tetrachloride	1.592	153.84	0.1624	7.28	0.09	0.0009
Trichloroethylene	1.462	131.40	0.1625	8.52	0.11	0.0010
1,1,2-Trichloroethane	1.435	133.42	0.1627	8.41	0.10	0.0010
Tetrachloroethylene	1.623	165.85	0.1625	6.76	0.08	0.0008
Chlorobenzene	1.106	112.56	0.1628	9.97	0.12	0.0012

by the sorbent tube. Sampling rates were determined for 1-, 2-, 4-, 8-, and 16-hr exposures at concentrations of 1, 10, and 100 ppbv. The dosimeters were exposed in triplicate under each test condition and the exposure chamber was sampled during each trial with active sampling tubes to validate compound concentration within the chamber. When both diffusion surfaces are exposed, the average equivalent sampling rate as determined by this procedure is ~ 50 cm^3/min.

Calibration curves generated from plots of the dosimeter loading vs the product of concentration and exposure time (C x t) may be used to determine the air levels of specific chemicals in field exposures. Calibration curves for the least and most volatile compounds (chlorobenzene and chloroform, repectively) studied are shown in Figure 8. Linear responses were obtained for all compounds tested in the 1 to 100 ppbv air concentration range. Prelimininary data indicate that equivalent sampling rates for higher levels of the more volatile compounds decrease as exposure times are increased (see Figure 9). This behavior appears to be consistent with the theory of reversible sorption (see Introduction).

A major advantage of the MRC monitor over the charcoal-based commercial devices discussed earlier is the greatly enhanced sensitivity achieved by thermal desorption. When solvent desorption is required, less than 0.5% of the collected sample can

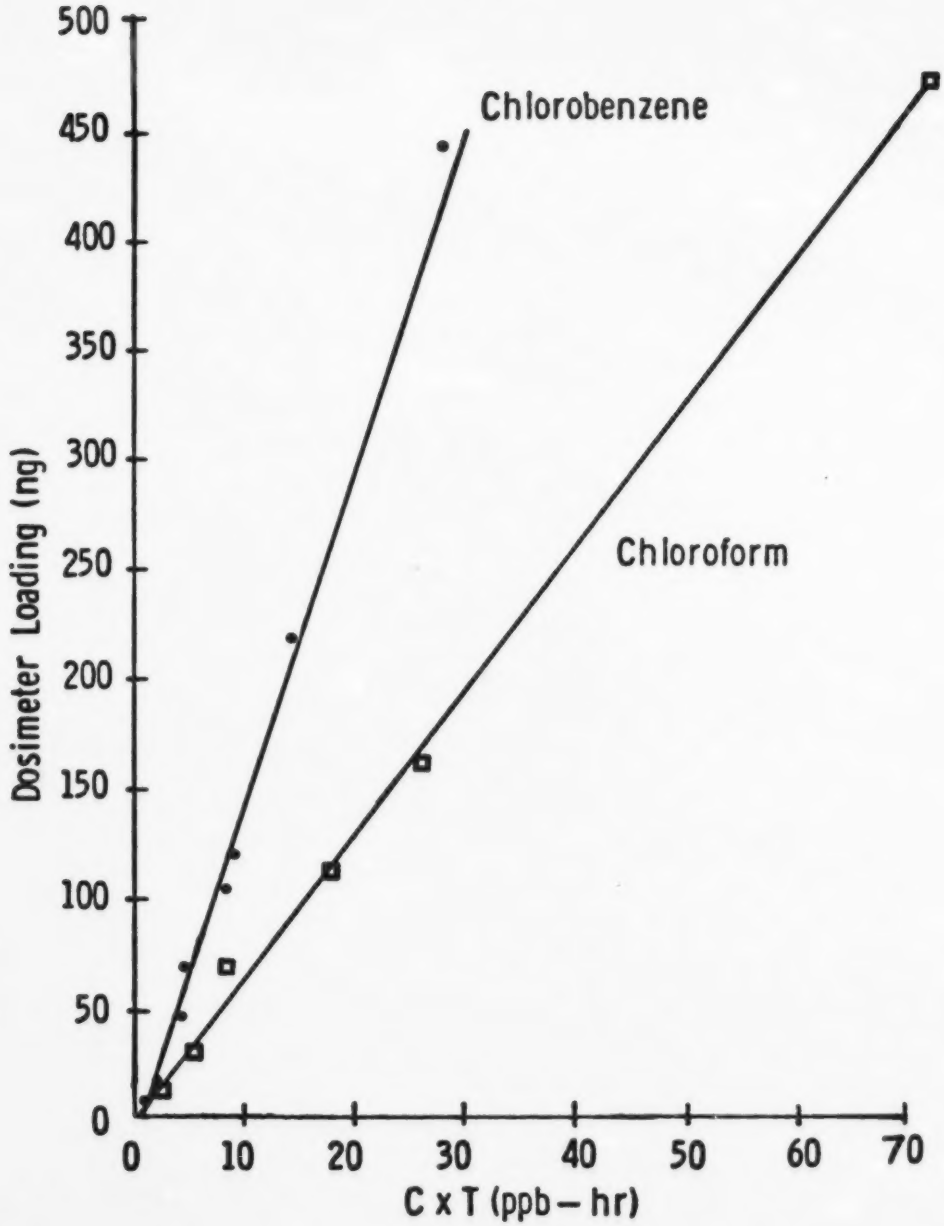


Figure 8. Dose response of MRC monitor to least and most volatile chemical tested.

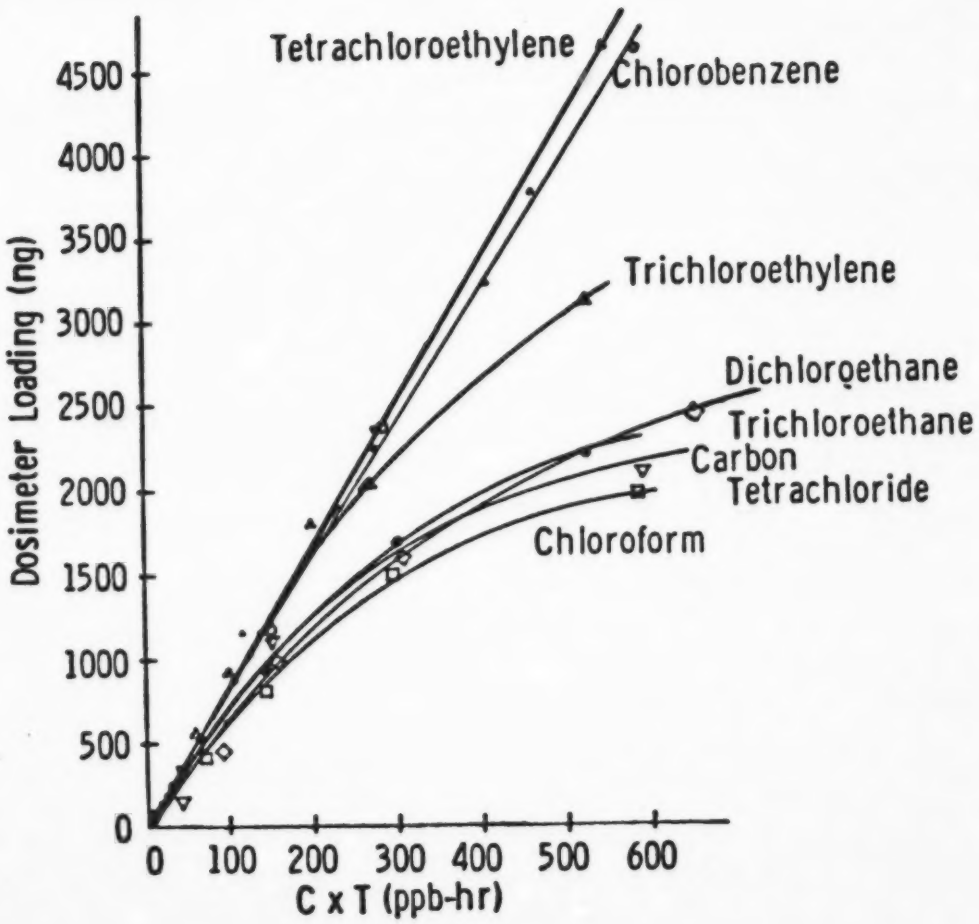


Figure 9. Response of MRC dosimeter at long exposure times.

be analyzed (e.g., 5 L of 1 mL extraction solvent). Thermal desorption and analysis of the entire sample affords a 200-fold (or greater) increase in sensitivity, permitting the measurement of parts-per-billion concentrations with less than 1-hr exposure times. Data from single-face, 1-hr exposures to ~ 10 ppb levels of seven volatile organic compounds are given in Table IX. Similar results are presented in Table X for 45-min dual-face exposures. As is shown in these tables, good recoveries were obtained for all compounds and good tube/dosimeter correlation was noted in each case. A high blank reading was observed for tetrachloroethylene, which accounts for the greater variance between tube and dosimeter analyses.

Further chamber studies were undertaken to demonstrate the effects of fluctuating concentrations of air pollutants on the MRC dosimeter response. In these experiments, the syringe drive rate on the sample generation system was varied over the exposure time, thus varying the chamber gas concentrations. An active sampling tube was used to sample the exposure chamber during the test to verify concentrations. Concentrations were varied from 1 to 10 to 100 ppbv. Results of these experiments are shown in Table XI. Sampling performance was equivalent to that demonstrated at constant concentrations.

Table IX. MRC dosimeter single face sampling for one hour

Compound	Concentration (ppb)		Percent recovery	Concentration (ppb)	Ratio dosimeter/ tube
	Theory	Tube		Dosimeter	
Chloroform	11.6	11.1	96	12.9	1.17
1,2-Dichloroethane	13.7	13.7	100	13.8	1.00
Carbon tetrachloride	8.8	10.6	120	9.7	0.91
Trichloroethylene	10.4	10.2	98	12.1	1.19
1,1,2-Trichloroethane	10.2	11.1	109	12.5	1.13
Tetrachloroethylene	8.2	8.6	105	13.7	1.59
Chlorobenzene	12.1	11.0	91	12.4	1.13

Table X. MRC dosimeter dual face sampling for 45 minutes

Compound	Concentration (ppb)		Percent recovery	Concentration (ppb)	Ratio dosimeter/ tube
	Theory	Tube		Dosimeter	
Chloroform	11.6	11.5	100	8.7	0.76
1,2-Dichloroethane	13.9	14.0	100	9.1	0.65
Carbon tetrachloride	9.0	11.7	130	8.9	0.76
Trichloroethylene	10.5	9.8	93	9.6	0.98
1,1,2-Trichloroethane	10.3	10.6	103	10.3	0.97
Tetrachloroethylene	8.3	8.5	102	10.6	1.25
Chlorobenzene	12.3	9.5	77	11.2	1.18

Table XI. MRC dosimeter response to fluctuating concentrations (dual face sampling for one hour)[a]

Compound	Concentration (ppb) Theory	Concentration (ppb) Tube	Percent recovery	Concentration (ppb) Dosimeter	Ratio dosimeter/ tube
Chloroform	22	22.7	103	23.9	1.05
1,2-Dichloroethane	26.6	26.6	100	24.7	0.93
Carbon tetrachloride	17.0	21.3	125	20.5	0.96
Trichloroethylene	20.0	20.9	105	25.0	1.20
1,1,2-Trichloroethane	19.7	21.5	109	24.7	1.15
Tetrachloroethylene	15.8	16.6	105	24.5	1.48
Chlorobenzene	23.4	24.4	104	25.3	1.04

[a]1 ppb - 40 min; 10 ppb - 10 min; 100 ppb - 10 min. (approximate concentrations).

The effects of air velocity on the MRC dosimeter performance were studied under laboratory and field conditions. In laboratory tests, air flow rates of 300 cm^3/min and 3.5 L/min through the 2 L exposure chamber gave equivalent sampling rates. However, studies conducted under carefully controlled conditions in the 200 L chamber described earlier showed that the sampling rates for the MRC device under a linear face velocity of 50 cm/s (1 mph) were on the average 64% of those obtained at 500 cm/s (10 mph). These empirical results agreed almost exactly with predictions based on the boundary layer theory previously discussed. Under field sampling conditions, dosimeters oriented with faces normal and at right angles to wind direction gave similar results. Wind velocities up to 900 cm/s (20 mph) were encountered during this study. Humidity and temperature effects were also of little or no consequence as indicated by the field studies. Temperatures of ~90°F and relative humidities as high as 80% during the test period did not seem to affect dosimeter performance. Controlled laboratory evaluations at 87% and 92% relative humidities likewise showed little or no effects on sampling rates.

Additional field tests were conducted during the winter months. Five dosimeters were exposed for 1 hr each at sequential 1-hr intervals, while a sixth dosimeter was exposed continuously for 5 hr. Samples were also collected with active Tenax tubes for

1 hr each during the first, third and fifth hours. Two additional dosimeters were fortified in the laboratory to determine recoveries. One of the fortified dosimeters was exposed for 1 hr during the fifth interval. A summary of the field results are presented in Table XII. Excellent agreement between the results for passive and active monitors was obtained for all chemicals measured.

For another field test, the MRC passive dosimeter and NIOSH charcoal tubes were used simultaneously to sample 1,2-dichloroethane in a chemical manufacturing plant. Results are given in Table XIII. Even at these very high air concentrations, good agreement was achieved between the charcoal tubes and the passive device with one exception. This may have been due to the position of the MRC dosimeter with respect to the charcoal sampling tube; the former was shielded by protective clothing, thus minimizing the overall exposure. However, the possibility of reduced response due to overloading (reversible sorption) of the MRC device cannot be dismissed.

Tests to determine the effectiveness of packaging to prevent contamination of the MRC dosimeters were also conducted. Friction-tight linear polyethylene caps (Caplug® Nos.EC-24 and WW-18) were used to seal off the open ends of the dosimeters (the larger cap fitted over the sides of the smaller cap). The capped dosimeters were then placed into sealed friction-lid metal cans (paint can type). These cans were pretreated by baking in an

Table XII. Field exposure of MRC dosimeter

Compound	CxT (ppb-hr)						
	Dosimeter sample interval						5 hr exposure
	1 hr	2 hr	3 hr	4 hr	5 hr	Σ	
Passive dosimeter							
Chloroform	-	-	-	-	-	-	-
1,2-Dichloroethane	0.27	0.29	0.24	0.20	~0.10	~1.1	0.67
Carbon tetrachloride	-	-	-	-	-	-	-
Trichloroethylene	0.58	0.38	0.25	0.11	0.16	1.48	1.47
1,1,2-Trichloroethane	0.16	0.48	-	0.38	0.48	1.50	0.90
Tetrachloroethylene	0.25	0.38	-	0.15	0.12	0.90	0.66
Chlorobenzene	8.4	18.2	10.4	8.6	6.7	51.0	51.0
Pumped tube (28 cm^3/min)							
Chloroform	-		-		-		
1,2-Dichloroethane	0.34		0.14		0.13		
Carbon tetrachloride	-		-		-		
Trichloroethylene	0.43		0.22		0.15		
1,1,2-Trichloroethane	0.49		-		0.59		
Tetrachloroethylene	0.11		-		0.17		
Chlorobenzene	7.5		9.6		5.4		

[a]Temperature ≈ -12°C; wind velocity ≈ 220 cm/s (5 mph).

Table XIII. 1,2-Dichloroethane sampling with active charcoal tubes and MRC passive monitors

Charcoal tube	#1	#2	#3	#4
Flow rate (ml/min)	47.2	46.2	50.2	49.0
Loading (µg)	81	456	305	17,865
Exposure time (hr)	5.6	5.6	5.6	5.6
Concentration (µg/L)	5.1	27.8	18.2	1,027
(ppm)	1.3	6.9	4.5	254
Dosimeter	**#90**	**#91**	**#92**	**#93**
Equivalent (ml/min) pump rate	30.0	30.0	30.0	30.0
Loading (µg)	64.0	277	212	1,536
Exposure time (hr)	5.6	5.6	5.6	5.6
Concentration (µg/L)	6.3	25.9	21.0	144.0
(ppm)	1.6	6.4	5.2	35.6

Table XIV. MRC dosimeter storage stability

Compound	Initial loading (ng)	Loading after 12 days (ng)	Loss (%)
Chloroform	25.0	22.4	10
1,2-Dichloroethane	23.3	21.0	10
Carbon tetrachloride	21.0	10.5	50
Trichloroethylene	24.3	20.0	18
1,1,2-Trichloroethane	27.5	23.2	16
Tetrachloroethylene	29.7	26.6	10
Chlorobenzene	32.1	27.0	15

oven at 250°C for 2-4 hr to remove volatile organics from the metal surfaces. An activated charcoal cartridge was also placed in the can to preferentially sorb organic contaminants during storage. Dosimeter background levels were not changed significantly by up to 4-week exposures of the package to laboratory environments.

A cursory study was conducted to determine the extent of compound loss during storage. Initial storage tests involved exposing a series of dosimeters to the test gas mixture at 1 ppb and observing compound recovery with respect to time. Replicate dosimeters were analyzed initially to establish the concentrations at the beginning of storage. The remainder of the dosimeters were capped with friction-tight caps, placed in screw-cap glass jars, and maintained at ambient laboratory conditions for 12 days. Results of this study are given in Table XIV.

As indicated by the results in the table, significant losses were observed only in the case of carbon tetrachloride which showed a decrease of 50% over the 12-day period. Losses of carbon tetrachloride may be due to chemical breakdown during storage or on the subsequent thermal desorption. Recoveries of other compounds were at acceptable levels, but may be improved by packaging and environmental controls.

SUMMARY

The duPont Pro-Tek® G-AA organic vapor badge may be applied to 24-hr monitoring of benzene and volatile chlorinated organic compounds at ambient atmospheric levels (ppb) when appropriate care is taken during manufacture to limit background contamination. While published sampling rates are generally acceptable for the compounds examined, consistently low values were obtained for carbon tetrachloride. This, along with badge-to-badge variations in sampling rates, may present problems if the devices are to be used to obtain quantitative data. Relative humidities in excess of 75 to 80% and poor air circulation seriously reduce the effective sampling rates of the duPont devices. Therefore, if duPont devices are used, air velocity and humidity effects should be considered carefully.

The Monsanto Research Corporation passive dosimeter is thermally desorbable and is more sensitive than the duPont badge. When hydrophobic sorbents such as Tenax GC are used, atmospheric humidity has little or no effect on performance. The MRC device can monitor benzene and chlorinated organics at ppb levels with only short (< 1 hr) exposure times. However, its use for long-term (e.g. 24-hr) sampling of the more volatile organics may be limited by reversible sorption problems.

References

1. Budiansky, S. (1980) Environ. Sci. Technol. 14: 1023-1027.
2. Wallace, L.A. and Ott, W.R. (1982) J. Air Poll. Contr. Assoc. 32: 601-610.
3. Coulson, D.M., Selover, S.J., Gunderson, E.C., and Kingsley, B.A., (1982) "Diffusional Sampling for Toxic Substances", 184th National Meeting of the American Chemical Society, Kansas City, MO. paper no. ENVR 32.
4. Coker, D.T. (1981) In: "Detection and Measurement of Hazardous Gases", Cullis, C.F.; Finth, J.G. (Eds.), London: Heinemann, Chapter 5.
5. Rose, V.E. and Perkins, J.L. (1982) Am. Ind. Hyg. Assoc. J. 43: 605-621.
6. Coutant, R.W. and Scott, D.R. (1982) Environ. Sci. Technol. 16: 410-413.
7. Lautenberger, W.J., Kring, E.V., and Morello, J.A. (1980) Am. Ind. Hyg. Assoc. 41: 737-747.
8. Bird, R.B., Stewart, W.E., and Lightfoot, E.N. (1960) "Transport Phenomena", New York, NY: John Wiley and Sons, Inc., Chapter 4 and 19.
9. Fuller, E.N., Schettler, P.D., and Giddings, J.C. (1966) Ind. Eng. Chem. 58: 18-27.

10. Reid, R.C., Prausnitz, J.M., and Sherwood, T.K. (1977) "The Properties of Gases and Liquids; 3rd. Ed., New York, NY: McGraw Hill, p. 544 ff.